Senior Thesis

A Geochemical Evaluation of Water Quality Along the Course of the Huron River, Northern Ohio.

by
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Abstract

The principal source of water in the Huron River is groundwater. However, other water types also enter the river at various localities along the course of the river. The water in the Huron River consists of a mixture of two groundwater components as well as waters from other sources whose entry into the river changes the chemical composition of the water of the Huron River along its course.

Mixing and dilution occur along the entire course of the river. Initially the two groundwater components mix to form water reflecting both components. In addition, various contaminants enter the river and mix with the pristine water already in the river channel. Meteoric water serves as a diluting agent which decreases the concentrations of the elements dissolved in the water.

Contaminants enter the river in the form of sewage effluent and industrial waste discharged either directly or via tributary streams. How and to what extent these influxes of water affect the chemical composition of the river can be determined through the interpretation of chemical analyses of water along the river's course. By treating the water as a series of mixtures, we can determine the natural composition of the water without the effects of contamination.

Introduction

The Huron River is a typical river in North Central Ohio. Like all northern Ohio rivers, it empties into Lake Erie which is a very dilute body of water in contrast to the Huron River. The higher element concentrations in the river are the result of many processes taking place along the river's course.

The Huron River is less than 35 miles in length, and it flows across glacial sediment for most of its course. The river drains many small to moderate size towns and villages identified on Figure 1. The water in the river is not used for drinking because ample groundwater is available for that purpose. The primary source of water in the river is groundwater and the chemical composition of the water in the Huron River is determined primarily by the composition of the local groundwater. Like many streams and rivers in north central Ohio, the Huron River also serves as a collector of sewage effluent and industrial wastes. These contaminants affect the chemical composition and quality of water in the river.

One of the first major government-sponsored studies of Lake Erie was published in 1968 by the Federal Water Pollution Control Administration and was entitled Lake Erie Report. Since this time, many efforts have been made to prevent further contamination of the lake by its tributary rivers. In order to achieve these goals, stricter controls have been placed on the discharge of sewage effluent on most areas. A subsequent study on Lake Erie's tributaries

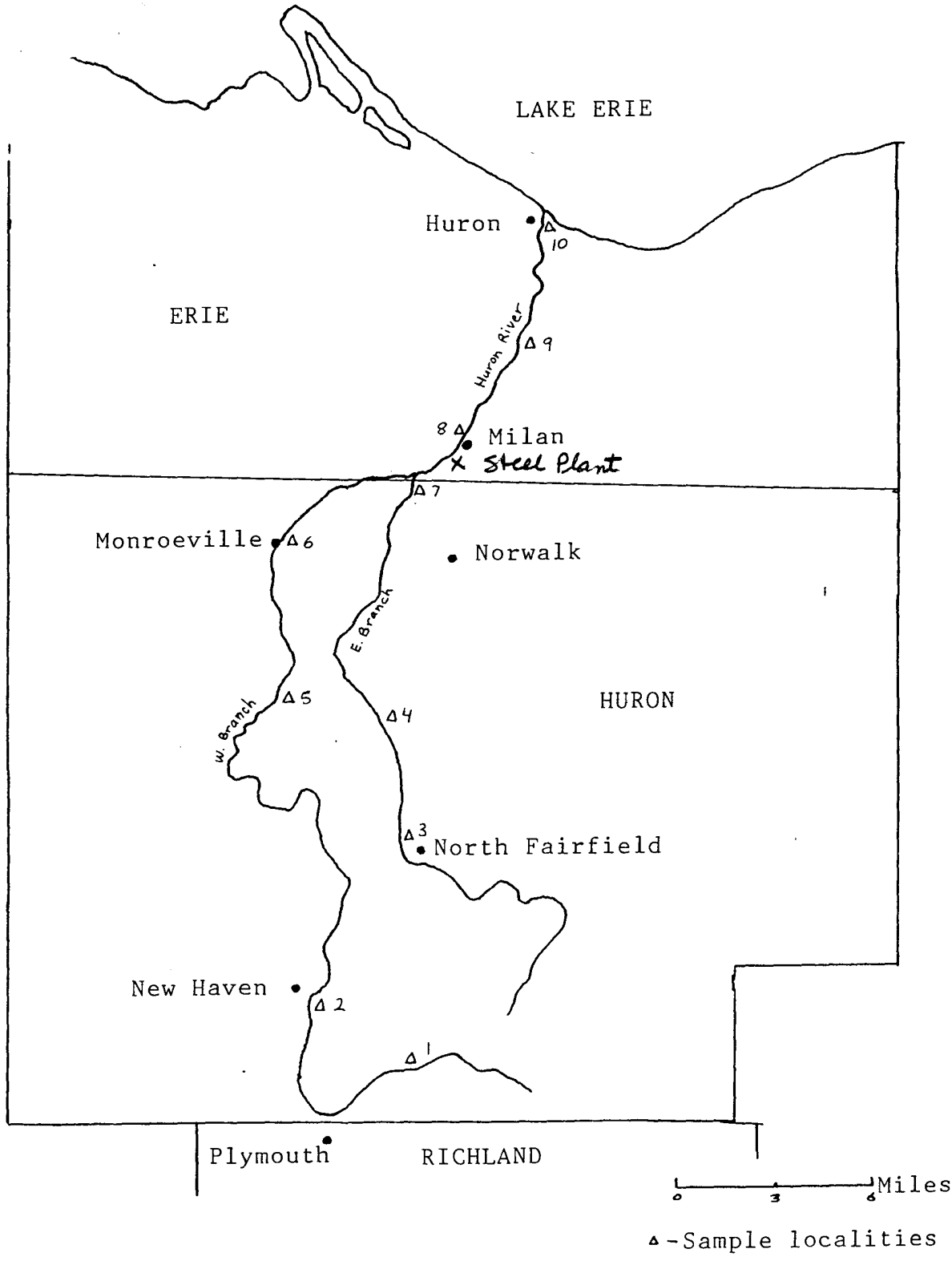


Fig. 1. Map of the drainage basin of the Huron River, northern Ohio.

was presented in 1980 by the Ohio E.P.A. in a publication entitled Ohio 1980 Water Quality Inventory. This study cites the improvements of Ohio's waters after the elimination of many rural sewage discharge sites and the improvement of old sewage disposal plants. Although many similar studies have dealt with sewage and phosphate disposal, the chemical composition of the Huron River over its entire length has not been studied before.

Sample Collection and Analysis

Ten 250 mL water samples were collected in polyethylene bottles at ten locations along the course of the Huron River (Figure 1). The samples were collected on December 20, 1991, prior to the year's first major snowfall. The locations are evenly distributed along the main branch and the two major tributary branches of the river (Fig.1). The samples were taken from the surface and near the banks of the river.

The water was acidified in the field to a pH = 2 with HNO3. The samples were stored at a temperature slightly below room temperature but were not refrigerated. Each sample was then filtered through 0.45 μm filters under vacuum. A small quantity of each sample was used to decontaminate the filtering equipment. The volume of each sample analyzed was 125 mL.

The analyses were done using Inductively Coupled Plasma

Spectrometry (ICP) by X-ray Assay Labs in Don Mills, Ontario. Each sample was analyzed for 25 elements including Na, K, Ca, and Mg. The detection limits of each element are listed in Table 1.

Table 2 displays the results of the analyses with the concentrations of the elements in parts per billion (μg/L). The following elements were not detected because their concentrations were below the detection limits: W, Bi, Sn, Sb, Zr, V, Co, Ag, Be. Several additional elements were detected in at least one sample in low concentrations, including: Pb, P, Mo, Cr, Ti, Ni, Cu, and Cd.

Variations Along the Course of the Huron River

The graphs of Figure 2 show how the concentrations of the most abundant elements vary along the course of the Huron River. Each graph has peaks and valleys which indicate influxes of water with unique but varying compositions. The graphs indicate that the two branches of the river have different concentrations of Ca, Na, Mg, and K. The concentrations of these elements are higher in the west branch than those in the east branch. Without accounting for the effects of dilution, one might assume that a major difference in chemical composition exists between the two branches.

Table 1. Detection limits of 25 selected elements using Inductively Coupled Plasma Spectrometry.

Element	Be	Na	Mg	P	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Sr	Zr	Mo	Ag	Cd	Sn	Sb	W	Pb	Bi
Detection Limit (ppb)	1	20	20	50	20	20	5	10	5	5	10	5	5	2	5	2	10	5	5	2	30	20	100	30	50

Table 2. Analytical data for water samples from the Huron River, Ohio, expressed in µg/L. Analyzed by X-Ray Assay Labs., Don Mills, Ontario, by ICP.

Element	1	2	3	4	5	6	7	8	9	10
Ca	61200	90700	56600	64300	88700	91900	37100	60800	80200	21900
Na	41000	36000	12600	9220	11700	15900	6690	14200	22700	5160
Mg	16800	25700	14600	13700	16900	22200	8980	12800	19500	5940
K	2500	3570	1910	1800	1990	2550	1430	2480	3120	860
Fe	358	259	107	212	149	158	63	81	522	167
Sr	790	753	488	209	465	504	116	268	372	97
Zn	n.d.	n.d.	46	67	30	10	72	80	11	n.d.
Mn	54	49	13	15	12	8	n.d.	7	33	11
Pb	n.d.	n.d.	n.d.	n.d.	45	n.d.	36	37	n.d.	n.d.
P	n.d.	209	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mo	16	n.d.	n.d.	9	n.d.	10	n.d.	n.d.	n.d.	n.d.
Cr	n.d.	n.d.	n.d.	10	n.d.	n.d.	n.d.	n.d.	n.d.	9
Ti	9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7	n.d.	n.d.
Cu	n.d.	n.d.	n.d.	4	n.d.	n.d.	n.d.	5	n.d.	3
Cd	n.d.	n.d.	3	5	n.d.	n.d.	n.d.	3	n.d.	n.d.

n.d. = not detected

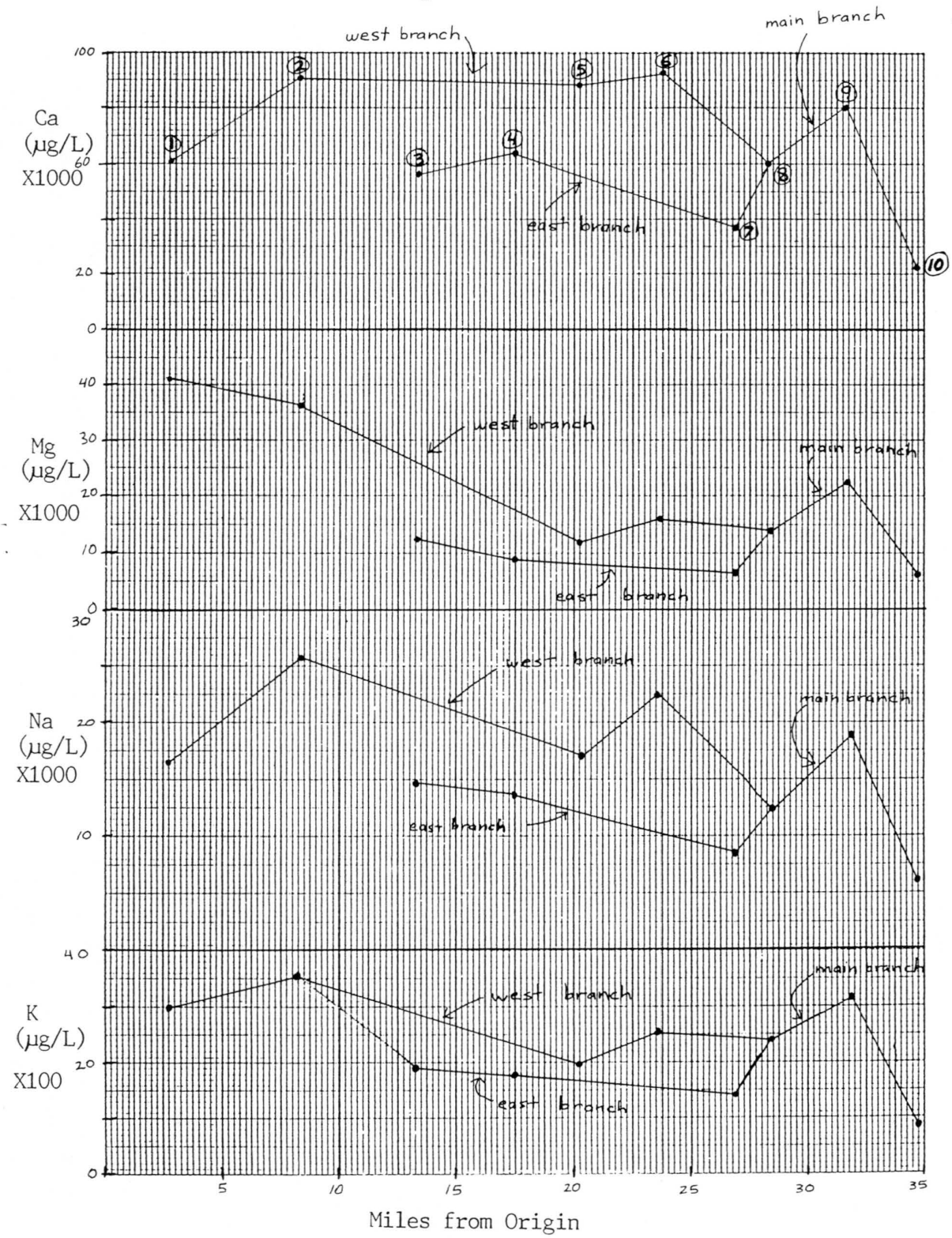


Fig. 2. Major element concentrations in µg/L along the course of the Huron River.

Mixing of the Branch Waters

From Figure 2 it can be determined that the chemical concentrations in each branch are different. Therefore, when the two branches join to form a single channel, a mixture of water from the two branches is formed. By using the data in Table 2 it is possible to determine the approximate volume fraction of water each branch contributes to the confluence water.

The concentrations of the four major elements were used in Equation 1, where A is the concentration and the subscripts e and w denote east/west branch, respectively. The subscript c indicates confluence water which is indicated by point 8 on Figure 2.

$$A_c = A_w f_w + A_e (1 - f_w) \qquad (1)$$

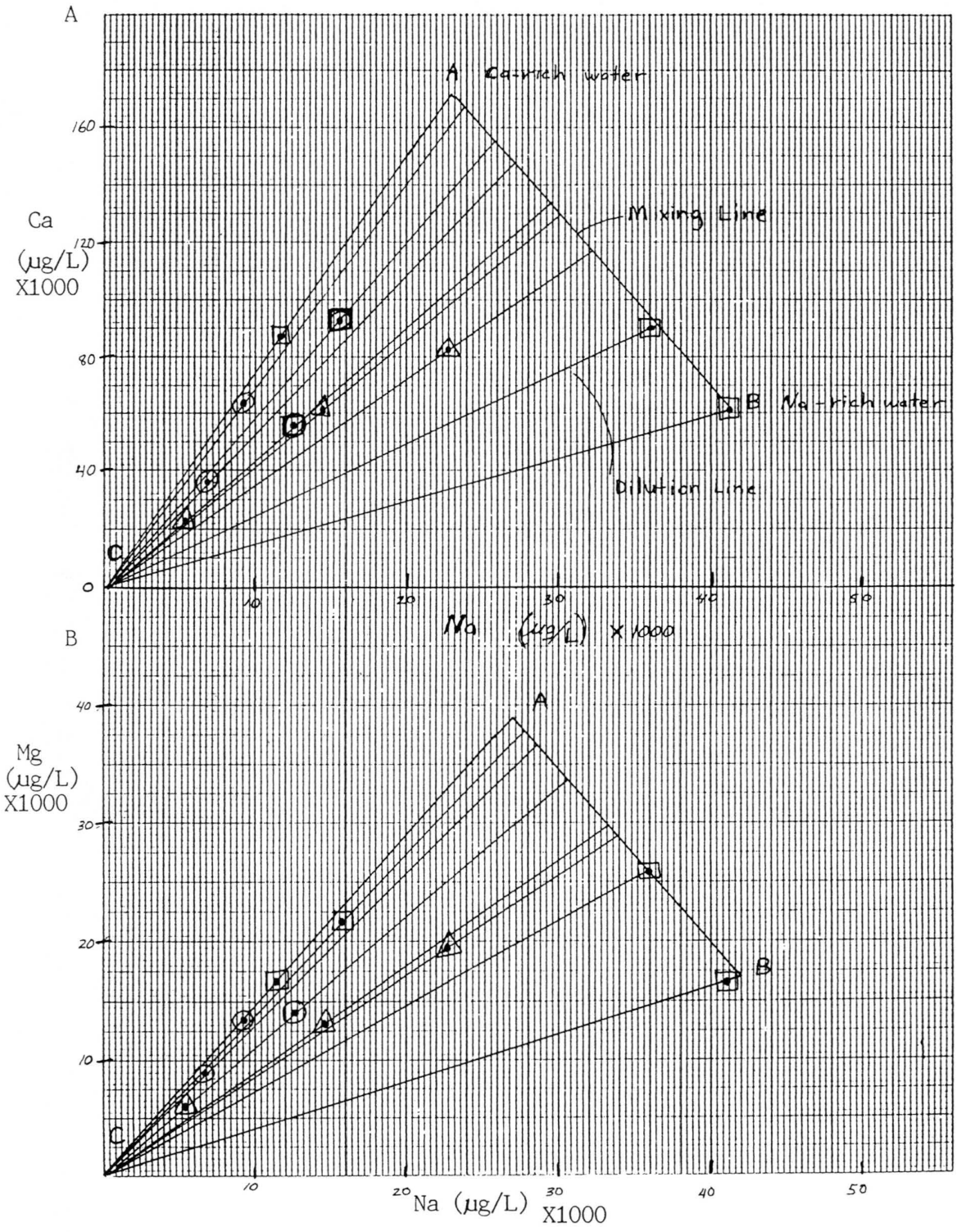
Solving for fw (volume fraction of the west branch), we get about 62% ± 15$\bar{\sigma}$ for the average of the major elements. This agrees with the stream discharges estimated by computing discharge from the length of each branch, which is assumed to be proportional to the area of the respective drainage basin. According to its length, the west branch should contribute about 60% of the volume of water at the confluence.

Mixing of Water Along the Course

Because the river water is a mixture of at least three sources of water, mixing triangles can be constructed using the major elements. These triangles (Fig.3) divide the groundwater into 2 components (A & B). Component A is Ca, Mg - rich and component B is Na - rich. A third component (C), present in the river, causes dilution and has the composition of meteoric water.

Calcium is most abundant among the major elements. In the west branch, the concentration of Ca remains nearly constant whereas in the east branch Ca concentrations fluctuate. The constant Ca concentration on the west branch suggests that dilution and groundwater type A enter at low and/or constant rates. Their input is such that they appear to cancel one another. However, a larger number of samples from the west branch may show fluctuations in the concentration of Ca. The variations of Ca in the east branch are likely caused by input of groundwater and surface run-off at varying rates. Sample #4 on Figure 2 indicates an influx of component A whereas sample #7 indicates that much dilution has taken place between the two samples.

The other three major elements exhibit different patterns of variation in each branch (Figure 2). The west branch has fluctuating concentrations, whereas the east branch shows a steady decrease in concentrations presumably



Fig, 3. Major element mixing triangles. A. Ca vs. Na. B. Mg vs. Na.

because of progressive dilution. Sample #5 is representative of type A water (high Ca, Mg, low Na) entering the river. In addition, dilution is occurring at location 5 as indicated by decreases in the concentrations primarily of Mg, Na, and K. Evidence to be presented later will demonstrate the input of component A at location 5 after the effects of dilution have been removed from the data.

Having looked at the samples individually, it is now appropriate to discuss the variations of the river as a whole. Figure 4, used in conjunction with Figure 2, allows us to recognize and to interpret patterns of chemical changes in the river. At the source of the river, groundwater of component B is accounting for most of the water. Here there is no component A and very little dilution. As the water progresses downstream, more and more of groundwater A enters the river and the dilution gradually increases as well. After location 5, there is an apparent shift in groundwater composition toward B, which continues until the branches come together to form a new source-water at location 8.

Mixing Below the Confluence

The sample taken at location 8 is a product of mixing of the two river branches. Figure 2 illustrates the effect of mixing the water of the two branches at location 8 below the confluence the concentration of each major element

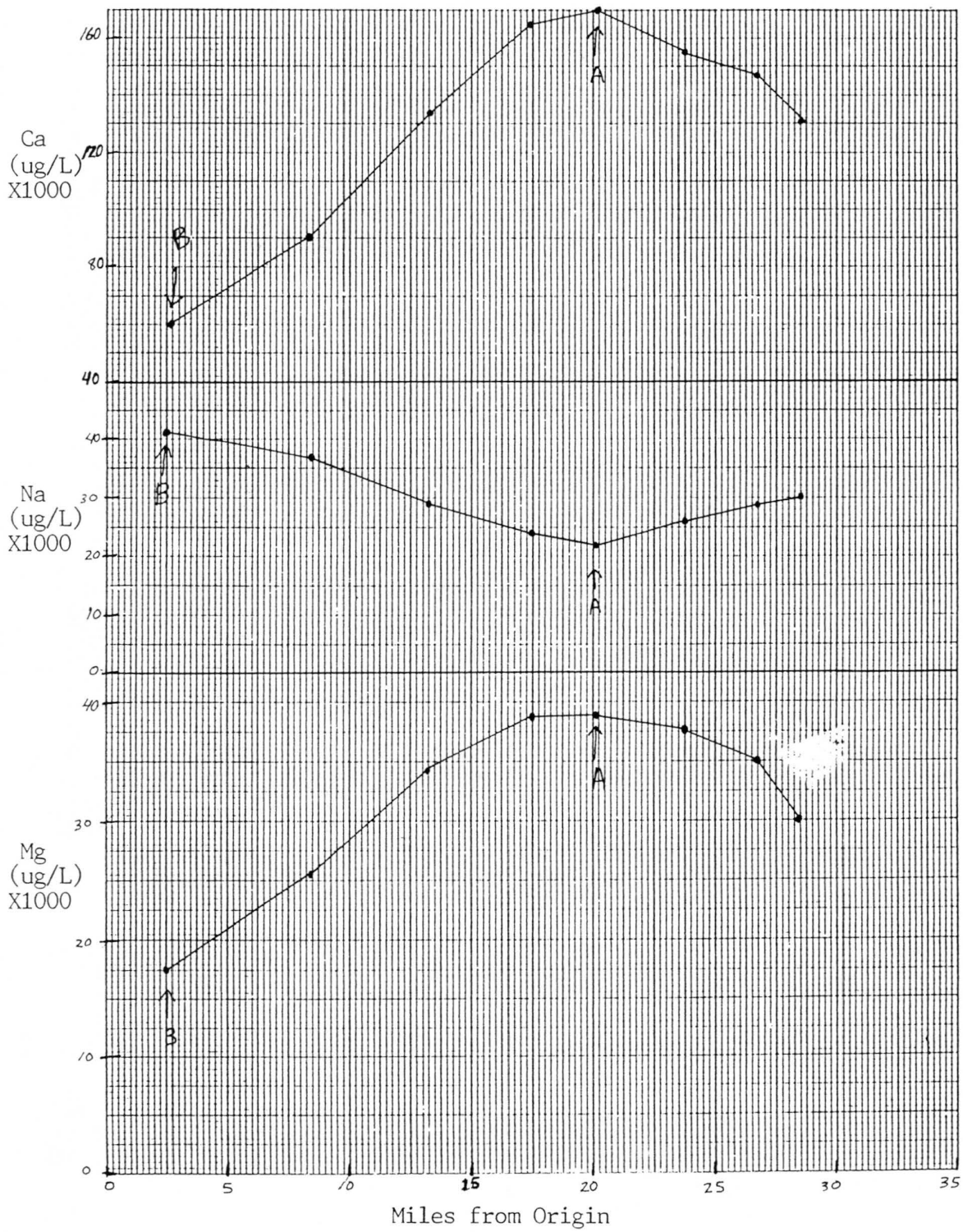


Fig. 4. Plots of major element concentrations with effects of dilution removed.

Table 3. Concentrations of major elements in µg/L without dilution.

Element	1	2	3	4	5	6	7
Ca	60000	90000	134000	165000	170000	155000	148000
Na	40000	38000	28000	24000	22500	26000	28000
Mg	17500	26000	34000	38000	38000	37500	35000

of sample #8 lies between the compositions of samples (6&7) taken from the east and west branches respectively.

The chemical composition of the waters of samples 9 and 10 downstream from the confluence are very distinctive. Sample #9 contains increased concentrations of the major elements followed by decreases in sample #10. This pattern of variation at the two locations is duplicated by most of the trace metals as well.

What is the reason for the high concentrations of metals in sample #9? One explanation is that highly concentrated groundwater may have entered the river between locations 8 and 9. By examining the Figures 3 and 4, I conclude that this is not the case. Because the concentrations of both Ca and Na increase, the contaminant cannot be water components A or B. Therefore, a new component, labeled D in Figure 5, must be present to account for the large increases in concentrations and is estimated to be a very undiluted point-source contaminant.

Upon discovering these abnormally high concencentrations at location 9, I investigated the situation further. What I found was that the high concentrations are likely to be the result of sewage effluent discharge. According to George

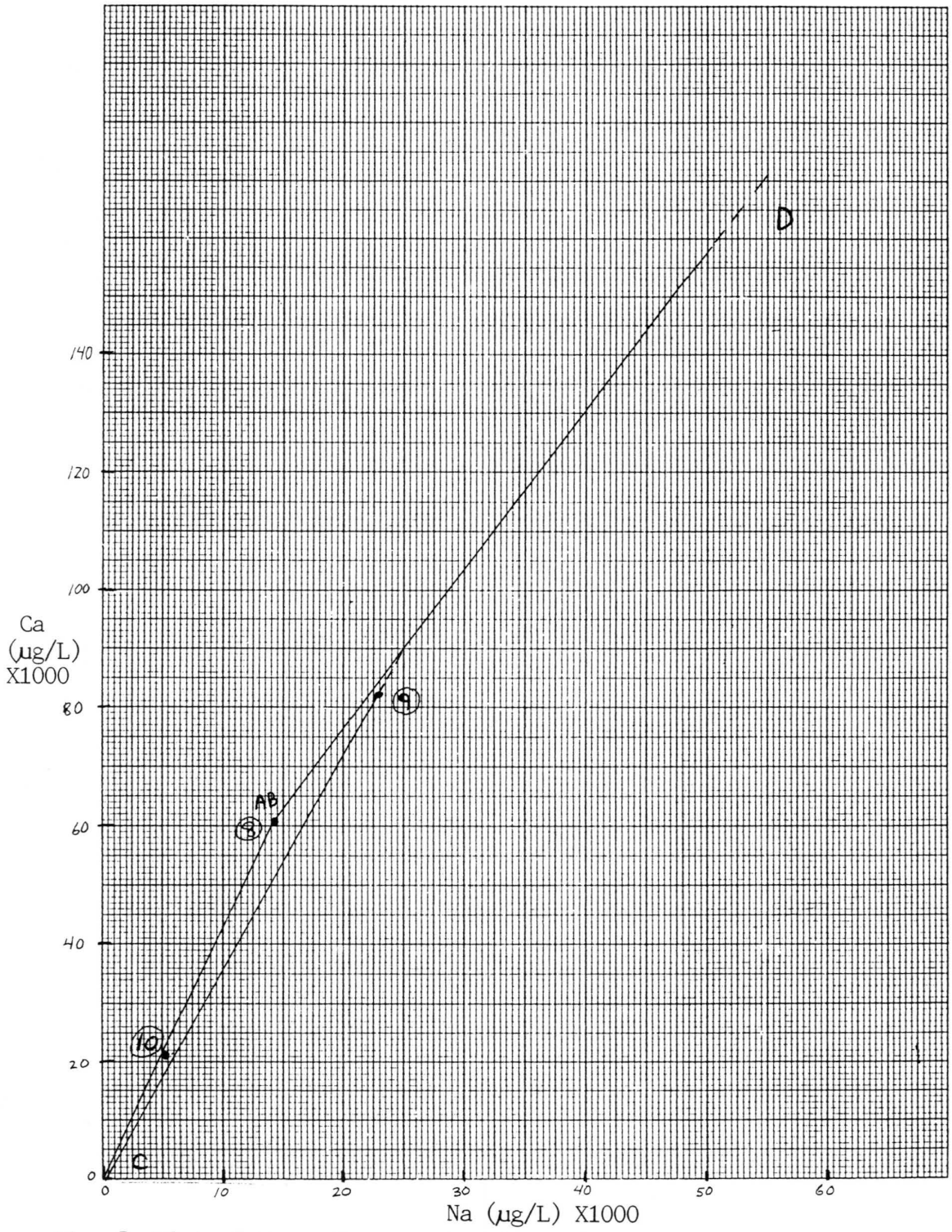


Fig. 5. Plot of Ca vs Na concentrations of samples 8,9,10. The diagram indicates the high concentrations of contaminant D.

Tigges of the Huron Basin Wastes & Hazards Management, domestic houses situated along the river at this location have poorly developed sewers and have been known to be responsible for discharge of raw sewage directly into the river. A municipal sewage treatment plant just north of Milan (Figure 6) discharges effluent into the river between points 8 and 9. However, Tigges stated that the concentrations of the discharged wastes at this locality are only at or below the concentrations of the natural river water.

Figure 5 is a mixing triangle describing very generally what the composition of component D must be in order to raise the concentrations of Ca and Na in the river to the levels present at location 9. Location 10 is near the mouth of the river within 150 m of Lake Erie and sample #10 is very dilute with respect to the major elements. Although the chemical composition of water from Lake Erie was not determined in this study, it is reasonable to conclude that sample #10 was diluted by mixing with the lake water. Dave Klarer of Old Woman Creek National Estuarine Preserve and State Nature Preserve determined concentration levels of near-shore Lake Erie water at different times in 1984/85. His data for near-shore Lake Erie water are approximately the same as concentration levels of sample #10. The comparison confirms that a large volume of lake water mixed with the river water at location 10.

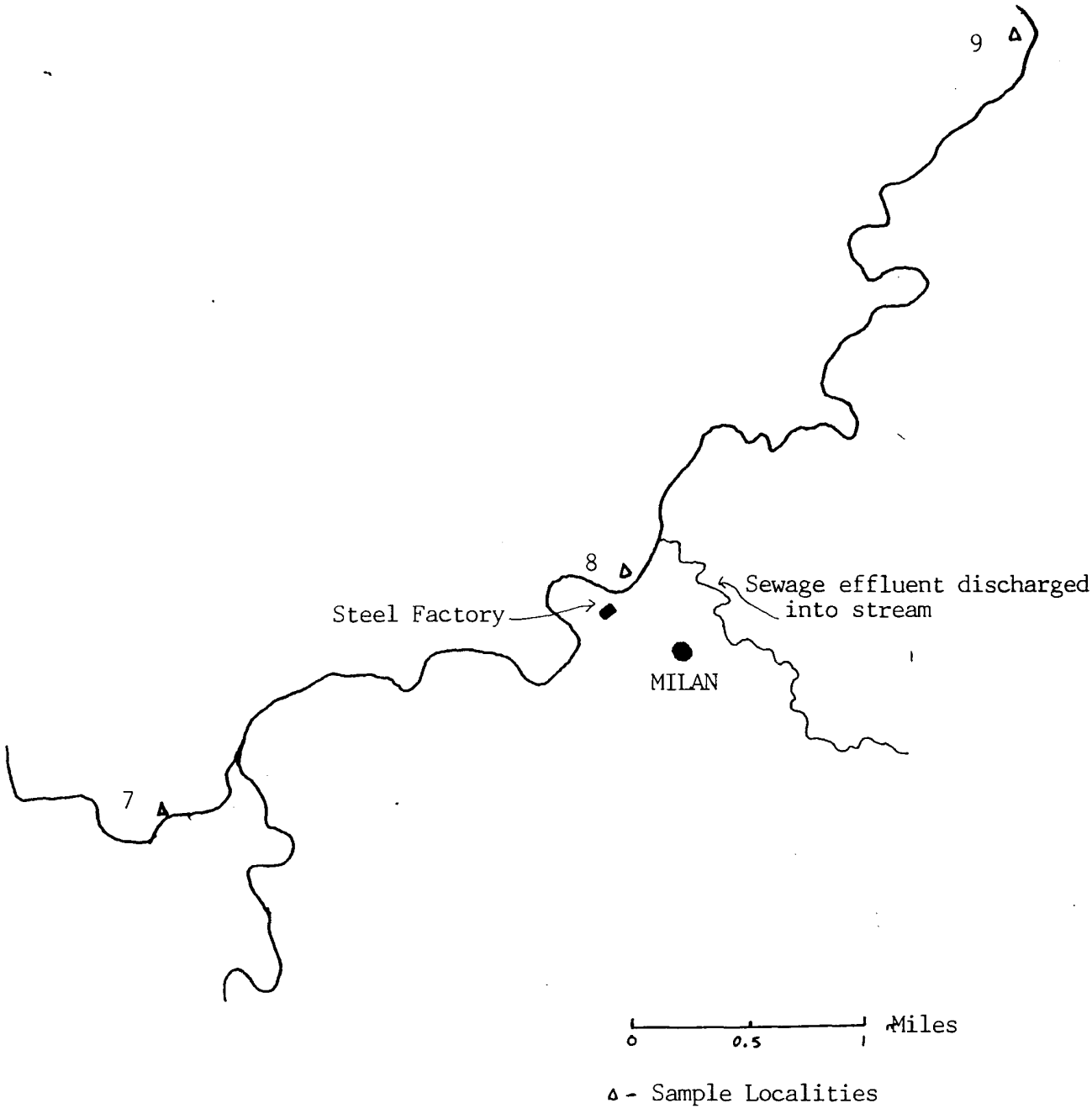


Fig. 6. Map of the Huron River near Milan,Ohio, showing the locations of three of the samples and sources of contamination.

Amount of Dilution

In order to determine the pristine nature of the source-water composing the two branches we must eliminate all effects of dilution. Dilution is caused by run-off of meteoric water. The mixing triangles of Figure 3 allow us to remove dilution effects by drawing dilution lines to the mixing line. By extending the dilution lines from the origin to the mixing line (AB) and transporrting the plotted points along these lines to the mixing line, the effects of dilution are removed

Figure 4 is based on the calculated results of how the concentrations of Ca, Na, and Mg would vary in terms of distance from the river's source if all dilution is removed. We can now see that there is no difference in the chemical composition of the groundwater of each branch of the Huron River. The apparent difference in composition seen in Figure 2 is caused by differences in the amount of dilution. The components making up the water below the confluence are not fully known; therefore, it is not possible to accurately remove the effects of dilution from these samples.

Trace Metals and Elements

In general, the primary trace metals, which consist of Fe, Sr, Zn, and Mn, follow the patterns set by the major elements with regards to relative element concentrations. The west branch of the river has consistently higher concen-

trations than the east branch, presumably again due to greater dilution in the east branch. Also following the pattern, the confluence water of sample #8 has concentration levels between the final levels of each branch, and water at location 9 shows an increase in trace metal concentrations. The only element which deviates from the pattern is Zn.

The Zn concentrations in the east branch are higher than those of the less dilute west branch. Even more surprising is the fact that the Zn concentration in sample #8 was higher than in any other sample, which is not consistent with the mixing model. Also, the concentration of Zn in sample #9 decreased when all other elements increased.

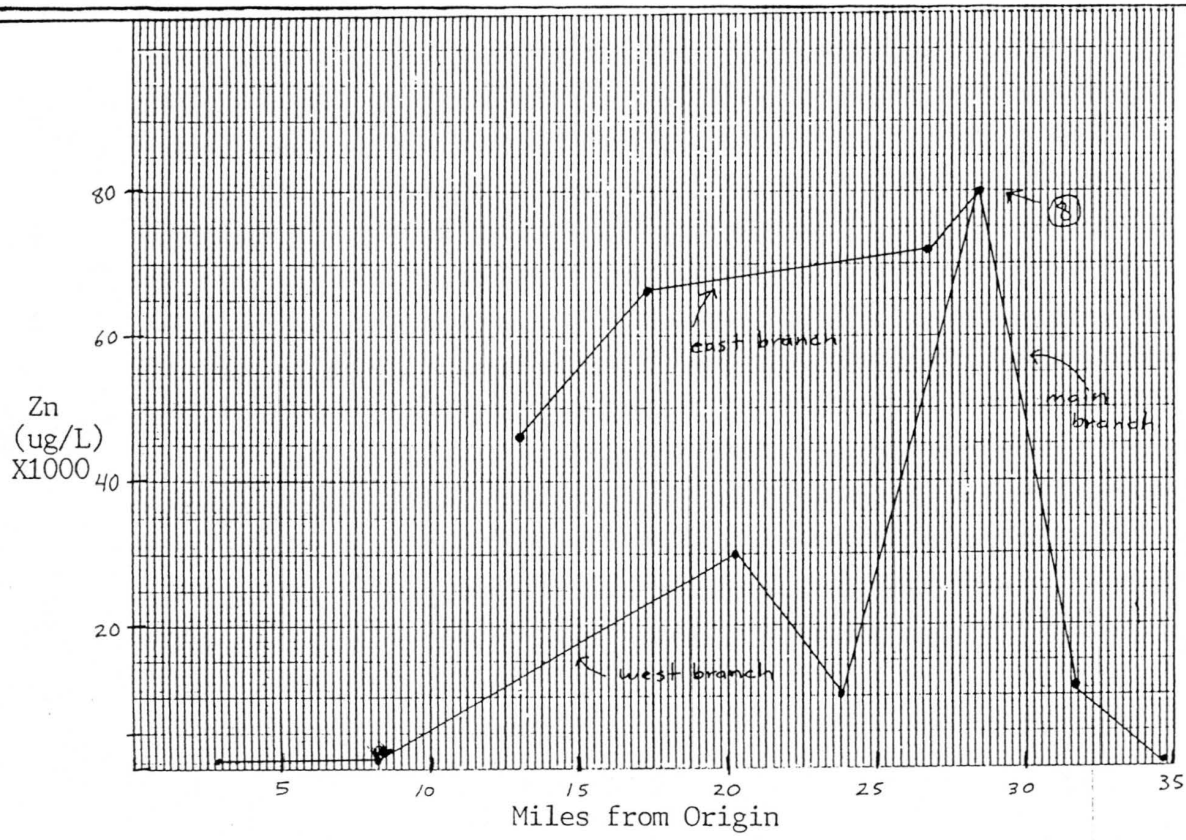


Fig. 7. Plot of Zn concentrations along the course of the Huron River.

The fact that the Zn concentration at location 8 increased at location 8 to a level higher than could be obtained by mixing proves that a major source of Zn in addition to groundwater is entering into the river. Figure 6 shows the location of a small steel plant in relation to the location of sample #8. Because the direction of water flow is northeast, there is strong reason to believe that the elevated Zn concentrations are due to waste discharge by the steel factory. In support of this hypothesis, Ni was also detected at the same location. Nickel is used to harden steel and was not detected at any other point along the Huron River.

Conclusions

The chemical composition of the Huron River reflects the many processes taking place along its course. By analyzing the river along its entire course we can determine the chemical composition of the source waters. If contamination from outside sources is excluded, it is possible to identify the locations of the inflows of different chemical components. We are then able to predict what the natural composition of the water would be without contamination.

Dilution is very important in the Huron River system. Meteoric water drains into the river and lowers the pristine concentration levels of water along the river. By removing dilution effects, we see that the two river branches are very

much a part of the same river system with related sources.

Knowing the composition of the natural waters allows us to locate the sources of contamination and the relative compositions of its components. The Huron River is a good example of how contaminants mix with natural waters to form a water with a composition different from both components. Thus, we can learn a lot from analyzing the chemical composition of our streams and throughout their course. In doing so we can detect contamination sources and do something about them in order to improve the water quality reaching the lakes and oceans.

Acknowledgements

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